

Analysis of the Plugging of the Systems Autonomy Demonstration Project Brassboard Filters

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ABSTRACT

There was a fine gray powder clogging the brassboard filters. The powder appeared to be residue from a galvanic corrosive attack by ammonia of the aluminum and stainless steel components in the system. The corrosion was caused by water and chlorine that had entered into the system and combined with the ammonia. This combination made an electrolyte and a corrosive agent of the ammonia that attacked the metals in the system. The corroded material traveled through the system with the ammonia and clogged the filters.

Key Conclusions were:

- The debris collecting in the filters is a by-product of galvanic Corrosion.
- The debris is principally corroded aluminum and stainless from the system.
- Galvanic Corrosion occurred from water and chlorine that entered the system during normal and/or extreme operating and servicing conditions.

Key Recommendations were:

- Use only one metal in the ammonia system -- titanium, aluminum or stainless steel.
- Make the system as air-tight as possible -- replace fittings with welded joints and replace EPR O-rings with Neoprene O-rings.
- Do not use freon to clean components in the system.

1.0 INTRODUCTION

The Systems Autonomy Demonstration Project is an effort to demonstrate the ability of a computer system to autonomously operate, monitor, and fault diagnose a prototype space station life support ammonia refrigeration system, the SADP TCS Brassboard. In the operation of the brassboard, the brassboard filters began to clog unexpectedly. After cleaning the filters, the brassboard was put back into operation. Yet, in a short time the problem had reoccurred.

1.1 Objectives

The analysis from this report is an effort as part of an on going investigation to identify the problem, and to resolve it if possible.

1.2 Study Method

The analysis here is purely analytical in nature. This entailed: visual observations of a corroded aluminum condenser, a chemical analysis of the debris collected by the filters, and an in depth investigation of causes of this type of corrosion. This report is based on these findings added to previous knowledge of corrosion and a considerable amount of accumulated experience in the area of ammonia refrigeration systems by the staff at Clay Engineering.

2.0 INVESTIGATION

2.1 Operational Background

The brassboard was operated at Johnson Space Center (JSC) for some time without incident. At JSC the condenser cooling loop used freon as the working fluid. The brassboard was brought to Ames where the condenser cooling loop was converted to use a methanol-water mixture as the working fluid. The brassboard was first operated at Ames on Sat. May 14, 1988. The brassboard was operated at Ames routinely for some period of time, without incident.

Table. 1: Operation of the Sundstrand brassboard (see ref.1)

Date Filled	Date Emptied	Number of times ran	Total Operation time (hrs)	Idle time (hrs)	Total time filled with NH ₃ (hrs)
May 14,'88	May 16,'88	4	9	58	67
May 25,'88	June 1,'88	3	6	160	166
June 28,'88	Sept. 2,'88	13	24	1561	1585
Sept. 7, '88	Nov. 14,'88	30	67	1563	1630
-- Oct. 1988	-- Noticed reduced RFMD bearing flow				
-- Nov. 15,'88	-- Cleaned all the filters (with freon)				
	-- Condenser #2 removed (leaks)				
Nov. 15,'88	Dec. 22,'88	18	31	687	718
-- Dec. 28,'88	-- Cleaned filters #1, 2, 3, & 7 only (with alcohol)				
Dec. 29,'88	(to-date)	5	5	1490	1495

2.2 Observations

2.2.1 Inspection of filters

The plugging of the filters was first observed when a noticeable decrease in the RFMD bearing flow was noted in mid October, five months from the first start-up date at Ames. Upon the first observation of the decreased bearing flow, the flow was noted to continually decrease over time. The bearing flow has been noted to have reduced significantly in a single day's operation of the system, and after long periods of dormant inoperation of the system. The flow rate to the bearings continued to drop till it reached a critical level.

After a critical loss in the RFMD bearing flow, the filters were removed and inspected. The filters were found to be clogged with a fine gray powder. In addition, the aluminum washer seals, at the filter connection joints, were found to be severely pitted at the inner diameter where the ammonia contacted the aluminum seal. The filters were cleaned and re-installed with new aluminum seals. After cleaning the filters, the RFMD bearing flow was greatly improved,

putting it back at its original higher flow rate. Nevertheless, reduction in bearing flow commenced again immediately, and there has been a problem with the filters clogging from this debris ever since.

2.2.2 Inspection of Condenser #2

Also of a concern, Condenser #2 leaked ammonia to the atmosphere whenever it was cooled to a steady-state temperature of approximately 30 °F by the cooling cart but did not leak when at room temperature. (This started occurring approximately the same time as the filters started getting clogged.) In the investigation, condenser #2 was removed and taken apart to investigate the leak in the condenser. The condenser's EPR seals were found to leak. The seals were found to have insufficient O-ring squash, approximately 0.004 in. due to having permanently deformed by cold flow. It appears that the seals allowed the water-methanol coolant mixture to leak into the ammonia system as well as allowing ammonia to leak out to the environment.

The O-rings appeared to have an undersized cross section for the width and depth of the O-ring groove in the condenser. The cross sectional shape of the O-ring changed from a circle to a square with rounded corners. This plastic deformation is an inherent property of EPR and was exacerbated from a lack of lateral support from the side walls of the O-ring groove.

The O-rings appeared to have originally been 3/16 in. dia. cross section as specified in the design drawings. The O-ring grooves are considered by Clay's to be a good design for a standard size Parker O-ring #2-388. This is a nominal 3/16 in. diameter cross section (c.s.) which is actually 0.210 in. c.s., not the 0.188 in. c.s. specified in the condenser drawings. This change would provide more lateral support from the side walls of the O-ring grooves and a change to neoprene would reduce the amount of cold flow of the O-rings.

In addition, the condenser was found to have light corrosion pitting along the aluminum surfaces in contact with the ammonia. The pitted areas were not deeply pitted, but had the appearance of having been etched. Also, there was some yellow liquid found in between the condenser plates along the outer

perimeter of the O-ring seals. The fluid had the appearance of ethylene glycol anti-freeze.

3.0 BRASSBOARD MATERIALS

3.1 Chemical Analysis of the Debris

First, the gray powder residue was removed from the filters and sent to two labs for independent analysis, Sundstrand Aviation Mechanical and Lawrence Livermore National Laboratories. Their results were similar, with the major constituents being aluminum and stainless steel. Sundstrand's results: "Results indicate the contaminates consist primarily of aluminum (and some aluminum oxide) with lesser amounts of chloride, iron and nickel. A water soluble ammonium salt and 4% carbon were also present. A small percentage of minute metallic particles were visually observed in the gray amorphous-like debris" (see ref.2). Lawrence Livermore Lab's results: "Compound is mostly inorganic containing small amounts of carbon. Small amount of ammonia. Inorganics appear to be aluminum and stainless steel" (see ref. 3).

Table. 2: Compositions by weight of the Filter Debris and other materials on the brassboard (see ref. 3, 4, & 5; pp. 2, 548, 156 respectively).

<u>Debris & Possible Sources</u>				
<u>Corrosion</u>	<u>Aluminum</u>	<u>Stainless Steels</u>		<u>Other</u>
<u>Debris</u>	<u>type 6061-T6</u>	<u>type 304</u>	<u>type 316</u>	<u>Sources</u>
Al:	~36.0% --> 97-98.5% Al			
Cl:	~17.0% ----->			Freon
Ni:	~13.0% ----->	8-10.5% Ni	10-14% Ni	
Fe:	~10.0% ----->	66-71% Fe	62-69% Fe	
N:	~7.8% ----->			NH ₃ , N ₂
H:	~5.3% ----->			NH ₃
C:	~3.6% ----->	0.08% C	0.08% C	
Cu:	~1.0% --> 0.15-0.4 % Cu			
Cr, Pb	--> 0.04-0.35% Cr	18-20%Cr	16-18% Cr	
Mn, Zn < 1.0%	--> 0.15% Mn	2% Mn	2% Mn	

Since the composition of the debris has the same chemical elements as that of the other materials found in the brassboard while operated or during servicing procedures, the debris is believed to come from the brassboard and from materials associated with its operation and servicing.

3.2 Aluminum

Since the major component of the debris was aluminum, it will be the first subject of attention. Much of the brassboard is made from aluminum, including the evaporators, condenser, junction blocks, etc.

Aluminum and its alloys are generally considered to be corrosive resistant but under some conditions it can corrode. Aluminum owes its excellent corrosion resistance to the barrier oxide film that is bonded strongly to its surface and that, if damaged, re-forms immediately in most environments. (see ref. 4, p. 583)

A number of the components in the brassboard are made of type 6061-T6 aluminum alloy which is a member of the 6xxx wrought Alloy family which exhibits good corrosion resistance and has the following characteristics. Members of the 6xxx wrought alloy family have moderately high strength and very good resistance to corrosion which make the heat-treatable wrought alloys of the 6xxx series (aluminum-magnesium-silicon) highly suitable in various structural, building, marine, machinery, and process-equipment applications. Copper additions, which augment strength in many of these alloys, are limited to small amounts to minimize its effect on corrosion resistance. In general, the level of resistance decreases somewhat with increasing copper content. (see ref. 4, p. 586)

In an ammonia environment, aluminum and its copper-free alloys are resistant to dry, gaseous ammonia, even at elevated temperatures. Aluminum is rated as "Fully resistant" to anhydrous-dry ammonia and as having "Excellent resistance" to ammonia, liquid or gas. In the presence of small amounts of moisture, there is moderate action on aluminum. Aluminum and its alloys are rated "Unsatisfactory" for moist Ammonia gas. Aluminum is resistant to pure anhydrous liquid ammonia, but contaminants such as metallic iron cause pitting

(note: The analysis by Lawrence Livermore Labs found the debris to contain approx. 10 % Iron by weight). (see ref. 6, pp. 418, 534, 538, 551)

In commercial service, aluminum equipment has been rated as giving excellent service in refrigerating systems handling liquid ammonia containing up to 5% water. However, under certain condensing conditions, ammonia-steam mixtures have caused corrosion that did not decrease in time, with the corrosion having been confined to the heat transfer surfaces. Aluminum compressors, heat exchangers, evaporators, condensers, and piping are used in producing ammonia, and aluminum pressure vessels for its storage and transportation. (see ref. 6, p. 418)

3.3 Stainless Steel

The second major corrosion constituent appeared to be stainless steel. Much of the brassboard is made from stainless steel, including the tubing, valves, filters, accumulator, and other components.

Stainless steels are iron-base alloys containing at least 10.5% Cr. With increasing chromium content and the presence or absence of some ten to fifteen other elements, stainless steels can provide an extraordinary range of corrosion resistance by forming a passive film on the outer surface. Chromium (Cr) is the one element essential in forming a passive film. Higher chromium content greatly increases the stability of the passive film (see ref. 4, p.549, 550, 586).

However, processing difficulties and other factors tend to limit increases in chromium content; therefore, improved corrosion resistance is usually obtained by adding molybdenum (Mo). Molybdenum is particularly effective in increasing resistance to the initiation of pitting and crevice corrosion. (see ref. 4, p.549, 550, 586).

Most of the stainless steel components in the brassboard are made of AISI 304 or 316 Stainless Steel. Type 304 has 18.0 to 20.0 % Chromium, and type 316 has 16.0 to 18.0 % chromium along with 2.0 to 3.0 % Molybdenum for improved

corrosion resistance. Both type 304 and 316 are of the austenitic stainless steel family. (see ref. 4, p. 549)

Stainless steels have shown good resistance to dry-anhydrous ammonia (NH_3) and hydrous ammonia, ammonium hydroxide (NH_4OH), at all concentrations up to the boiling point (see ref 4, p. 559). Both types 304 and 316 are rated "Fully resistant" to Ammonia (Dry or Moist) at All Concentrations between 70-212 °F. (see ref. 6, p. 502) Three other sources consistently give types 304 and 316 the highest rating for corrosion resistance to anhydrous ammonia (dry and moist), rating them as "Fully resistant", "Excellent resistance", and as giving "Very good service". (see ref. 6, pp. 534, 538, 551 and ref. 7, pp. 66, 68)

4.0 BRASSBOARD CORROSION

Since both the aluminum and the stainless steel are individually given high marks for corrosion resistant to pure anhydrous ammonia, with stainless steel also resistant to hydrous ammonia when in separate, isolated systems; there appears to be some other mechanism that is causing corrosion of the brassboard materials. The mechanism appears to be galvanic corrosion due to a galvanic coupling between the two dissimilar metals in the system.

4.1 Galvanic Corrosion within the brassboard

The combination of dissimilar metals in engineering design is quite common -- for example in heat exchangers, and machinery. Such combinations often lead to galvanic corrosion. Galvanic corrosion occurs when a metal or alloy is electrically coupled to another metal in the same electrolyte. The three essential components for galvanic corrosion are (see ref. 4, p. 83):

- Materials possessing different surface/voltage potential
- A common electrolyte
- A common electrical path

(1) Aluminum alloys and stainless steels do possess significantly different voltage potentials as given by the galvanic/electromotive force (emf) series.

(2) A common electrolyte will exist between the aluminum and the stainless steel if any, even very small amounts, of water were to have entered into the pure anhydrous ammonia in the system and contaminated it. (3) A common electrical path naturally occurs from the metal-to-metal connections of the many tubes, valves, condensers, evaporators, etc. Hence, there will be galvanic corrosion of the brassboard, as it currently exists, unless there is a complete absence of all traces of water and any other electrolyte contaminant when the brassboard is filled with ammonia.

Water could have been introduced into the system by several means. (1) Since there is moisture in the air, some water enters the system every time the sealed ammonia system is opened to the ambient air environment. (2) It is believed that condenser #2 may have leaked coolant (containing 50% water by volume) from the facility cooling cart into the ammonia side of the condenser. This occurred during pump-down evacuation of the ammonia system, prior to charging the system with ammonia. The condenser O-ring had only a few thousands of an inch squash when at room temperature. Then when cooled, the O-ring pulled away from the metal surfaces of the condenser due to a eight times greater coefficient of thermal expansion than aluminum.

Once inside, the water attaches itself to the metal walls inside the system and can be absorbed by the ammonia to produce Ammonium Hydroxide, a corrosive agent. Ammonium Hydroxide is known to be corrosive with aluminum, with small changes in the amount of water in the ammonia having the ability to cause significant changes in the corrosion rate.

Once inside, the water must be driven off to eliminate it from the system. To completely remove this, and any other source of water from the system, requires either pulling a high vacuum on the system while performing a "bake-out" to drive any traces of water out of the system, or a prolonged vacuum pump-down (several days) on a leak-tight system. In the latter case, it is particularly important that the system be leak tight or else moisture will be continually drawn into the system while under a vacuum.

Neither of these alternatives is simple, since neither of these methods can be readily performed here at Ames Research Center. There is a problem since

there is no easy access to a bake-out facility, and there are hundreds of fittings, each being a potential leak, creating an almost impossible task to make the brassboard a completely leak tight system. The difficulty lies in the fact that each fitting can leak just a minute amount but when multiplied by the number of fittings in the system, the leak rate for the system becomes far too great. (The best vacuum obtained in the brassboard, while at Ames, has been approximately 200 milliTorr, to date.)

5.0 GALVANIC CORROSION

Galvanic corrosion occurs when a metal or alloy is electrically coupled to another metal in the same electrolyte. There is a difference in voltage potential between dissimilar metals; this causes electron flow between them when they are electrically coupled in a conductive solution. The direction of flow, and therefore the galvanic behavior, depends on which metal or alloy is more active (see table 3). The material with the most negative, or anodic, corrosion potential (ie. the less corrosion-resistant metal) has a tendency to suffer accelerated corrosion when electrically connected to a material with a more positive, or noble, potential (the more corrosion-resistant metal). In the case of the brassboard, the aluminum acts as the anode and is corroded more rapidly, while the stainless steel acts as the cathode and is protected (corroded less rapidly). The driving force for the corrosion is the electrical potential established between the two metals, with the electron flow attempting to bring the two metals into equilibrium. (see ref. 4, pp. 83, 235)

The extent and rate of corrosion is affected by the potential difference between the metals, and the nature of both the environment and the metals involved. Pure anhydrous ammonia is electrically non-conductive, and will not support galvanic corrosion since it has high electrical resistance. But with only small additions of ions (ex. Chlorine, Iron, or other ions) the ammonia will act as an electrolyte. Small changes in the amount of electrolyte can change the driving potential of the reaction significantly when it is limited by high solution resistivity, ie. low electrical conductivity. Ammonia increases in electrical conductivity with increasing amounts of ions. Therefore, small changes in the amount of ions in the ammonia can cause significant changes in the corrosion rate by allowing greater amounts of current flow. (see ref. 4, p. 83, 235, 588)

**Table 3 Galvanic series in seawater
at 25 °C (77 °F) Source: Ref. 4, p. 83**

Corroded end (anodic, or least noble)	
	Magnesium
	Magnesium alloys
	Zinc
	Galvanized steel or galvanized wrought iron
*	Aluminum alloys
	5052, 3004, 3003, 1100, 6053, in this order
	Cadmium
	Aluminum alloys
	2117, 2017, 2024, in this order
	Low-carbon steel
	Wrought iron
	Cast iron
	Ni-Resist (high-nickel cast iron)
	Type 410 stainless steel (active)
	50-50 lead-tin solder
	Type 304 stainless steel (active)
	Type 316 stainless steel (active)
	Lead
	Tin
	Copper alloy C28000 (Muntz metal, 60% Cu)
	Copper alloy C67500 (manganese bronze A)
	Copper alloys C46400, C46500, C46600, C46700
	(naval brass)
	Nickel 200 (active)
	Inconel alloy 600 (active)
	Hastelloy alloy B
	Chlorimet 2
	Copper alloy C27000 (yellow brass, 65 % Cu)
	Copper alloys C44300, C44400, C44500
	(admiralty brass)
	Copper alloys C60800, C61400 (aluminum bronze)
	Copper alloy C23000 (red brass, 85% Cu)
	Copper C11000 (ETP copper)
	Copper alloys C65100, C65500 (silicon bronze)
	Copper alloy C71500 (copper nickel, 30% Ni)
	Copper alloy C92300, cast (lead-tin bronze G)
	Copper alloy C92200, cast (lead-tin bronze M)
	Nickel 200 (passive)
	Inconel alloy 600 (passive)
	Monel alloy 400
	Type 410 stainless steel (passive)
*	Type 304 stainless steel (passive)
*	Type 316 stainless steel (passive)
	Incoloy alloy 825
	Inconel alloy 625
	Hastelloy alloy C
	Chlorimet 3
	Silver
	Titanium
	Graphite
	Gold
	Platinum
Protected end (cathodic, or most noble)	

* Aluminum 6061, and Stainless steel types 304 and 316 are the most abundant metals in the system.

5.1 Galvanic Corrosion of Aluminum

Aluminum owes its excellent corrosion resistance to the oxide film that forms on its surface. However, the aluminum can only maintain good corrosion resistance through stability of its protective film. The film is stable only under certain environmental conditions. While the oxide film is stable over a pH range of about 4.0 to 9.0, it is soluble in most alkaline solutions and strong acids (see fig. 1). Within the passive pH range, about 4 to 9, aluminum alloys resist corrosion in solutions of most inorganic chemicals. Beyond the limits of its passive range, aluminum corrodes in aqueous solutions because its oxides are soluble in many acids and bases, yielding Al^{3+} ions in the former and AlO_2^- (aluminate) ions in the latter. (see ref. 4, p. 583; ref. 8, p. 6•64, 6•68)

Ammonium hydroxide (Ammonia and water) is alkaline with some variation in pH level depending on the ammonia to water concentration (see table 4). Any addition of water to anhydrous ammonia will create a pH level of about 10 pH or greater. The electric potential of 300 series stainless steel is -0.09 V, and that of 6061-T6 aluminum is -0.83 V for a combined potential of less than 1.00 Volt. In this environment, the oxide layer is attacked and cannot protect the aluminum metal underneath. As a result, the aluminum is corroded until the water in the system is consumed by the reaction. (see ref. 8, p. 6•68; and ref. 9, p. D-146.)

Table 4 Approximate pH Values	
Ammonia, 1N	11.6 pH
Ammonia, 0.1 N	11.1 pH
Ammonia, 0.01 N	10.6 pH

This can be anticipated since aluminum and its alloys occupy active positions in the galvanic series and are subject to failure by galvanic attack. Aluminum, as indicated by its position in the electromotive force (emf) series, is a thermodynamically reactive metal, particularly among structural metals (see table 3). "Under most environmental conditions frequently encountered in service, aluminum and its alloys are the anodes in galvanic cells with most other metals, protecting them by corroding sacrificially". Some aluminum alloys are even used for sacrificial anodes. (see ref. 4, pp. 84, 583, 587)

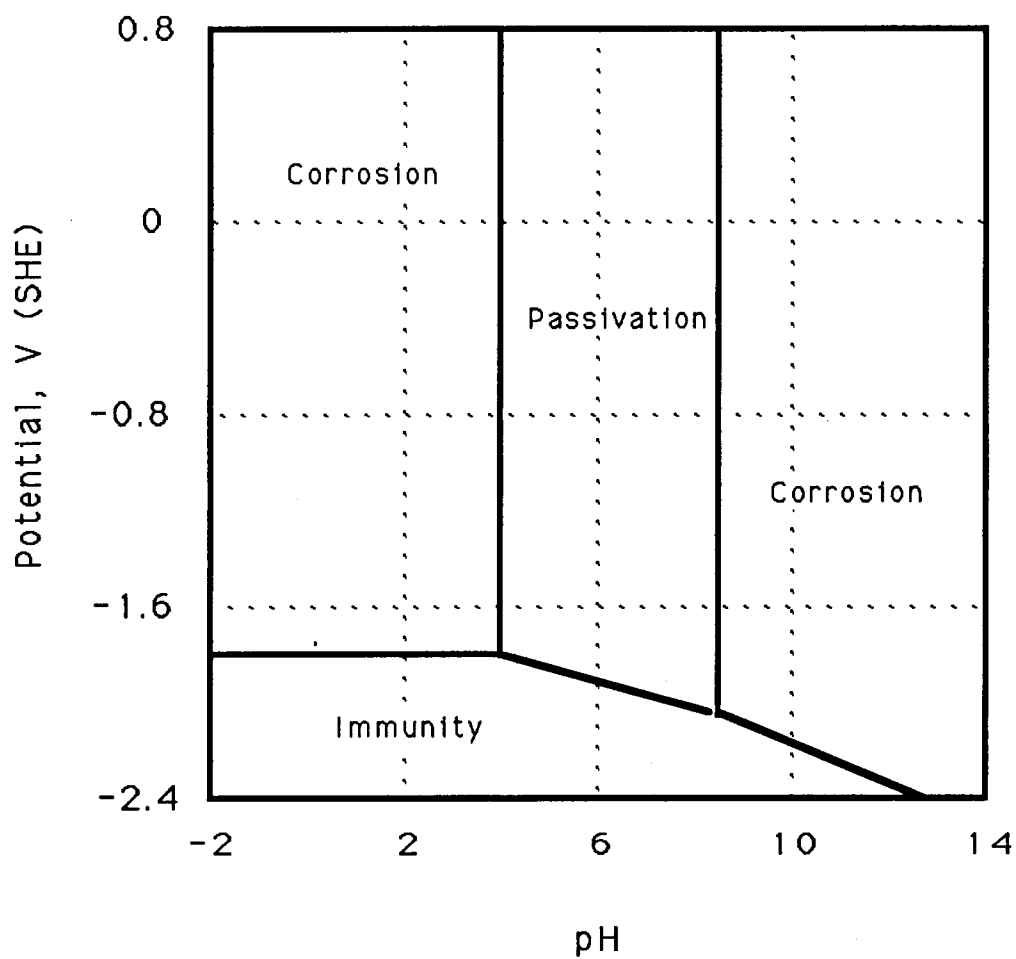


Fig. 1 Pourbaix diagram for aluminum with an $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ film at 25 °C (75 °F). Potential values are for the standard hydrogen electrode (SHE) scale. Source: see Ref. 10, p. 171.

"In many environments, aluminum can be used in contact with chromium or stainless steels with only slight acceleration of corrosion; chromium and stainless steels are easily polarized cathodically in mild environments, so that the corrosion current is small despite the large differences in the open-circuit potentials between these metals and aluminum" (see ref. 4, p. 587). Thus, the galvanic effects on aluminum, when coupled to stainless steel, tends to be minimized. Corrosion of aluminum in the passive range is localized, usually manifested by random formation of pits. The oxide ruptures at random weak points in the barrier layer and cannot repair itself, and localized corrosion develops at these points. Only when the cathodic reaction is sufficient to polarize the metal to its pitting potential will significant current flow and pitting corrosion start. And when localized corrosion such as pitting is possible in the galvanic couple, long induction periods may be required before these effects are observed. (see ref. 4, pp. 83, 84, 583)

Contact of aluminum with more cathodic metals should be avoided in any environment in which aluminum by itself is subject to pitting corrosion. Galvanic corrosion, although listed as one of the forms of corrosion, should instead be considered a type of corrosion mechanism, because anyone of the other forms of corrosion can be accelerated by galvanic effects. (see ref. 4, p. 234)

To minimize corrosion of aluminum wherever contact with more cathodic metals cannot be avoided, the ratio of the exposed surface area of the aluminum to that of the more cathodic metal (ie. stainless steel) should be as high as possible to minimize the rate of corrosion of the aluminum. (see ref. 4, p. 587)

5.1.1 Pitting Corrosion by Chlorine

Since there were definite visible signs of pitting of the aluminum in condenser #2, any possible causes for the pitting was investigated. For aluminum, pitting corrosion is most commonly produced by halite ions (column VII of the periodic chart), of which chloride (Cl^-) is the most frequently encountered in service (see ref. 4, p. 583). Noting that the debris found in the filters contained approx. 17 % Chlorine, it is believed that this could be a source of corrosion.

Pitting of aluminum by chloride ions is similar to galvanic corrosion, with the chloride ions making the ammonia an electrolyte. In chloride-bearing solutions, aluminum alloys are susceptible to galvanically induced localized corrosion, especially in dissimilar-metal crevices (ex. the aluminum seals for the filters). In this type of environment, severe galvanic effects are observed when aluminum alloys are coupled with more noble metals and alloys (ie. Stainless steel). However, in the absence of chlorides, aluminum and its alloys may be less active because of the greater stability of the protective oxide film. Galvanic effects are not as severe under these conditions. (see ref. 4, p. 84)

Austenitic stainless steels, such as types 304 and 316, are "very susceptible" to chloride pitting, also. Although, molybdenum-containing stainless steels, such as type 316 is more resistant than nonmolybdenum-containing alloys, such as type 304. However, most chloride environments require stainless steel alloys with greater amounts of chromium and molybdenum for better corrosion resistance. (see ref. 4, p. 84, 323)

It is believed that the chlorine found in the system was primarily introduced by the use of freon as a cleaning agent. Therefore, through the discontinued use of freon and any other chlorine bearing substances in the system, it is believed that this form of corrosion can be eliminated.

To improve this situation, (1) the chlorine containing solids were removed and the filters cleaned, (2) a cleaning agent was used to clean the filters other than freon, (3) the brassboard was repeatedly evacuated and purged with nitrogen to remove any remaining contaminant gases. However, the filters continued to become increasingly plugged since the removal of chlorides is extremely difficult in such a large system having: many feet of small diameter tubing, tiny orifices, crevices, needle valves, "Dead spots" with little or no flow-through (ie. Accumulator, BPRV liquid line), etc. From past experience of others, chlorine molecules have been seen remaining in an area for weeks after contact with freon (a chlorine containing agent), even after using cleaning methods to remove it.

5.1.2 Pitting Corrosion of Aluminum by other Ions

Other combinations of metals and corrosive fluids to avoid because of pitting tendencies are aluminum and aluminum alloys in electrolytes containing ions of such heavy metals as lead, copper, iron, and mercury (see ref. 4, p. 323).

In the debris sample there were significant amounts of iron, copper, and nickel which were at one time heavy metal ions, but are no longer due to the nature of the galvanic corrosion process.

5.2 Galvanic Corrosion of Stainless Steel

The galvanic corrosion behavior of stainless steels can be difficult to predict because of the dual position it has in the galvanic (emf) series. In this, stainless steels are unique from all other metals and alloys in that it exhibits two separate positions, or voltage potentials, within the galvanic series. However, aluminum is so anodic that it is always more anodic than stainless steel. Therefore stainless steel will have a noble position in the galvanic series and remain in a passive state while coupled with aluminum. (see ref. 4, p. 84).

The mechanism of corrosion protection for stainless steels differs from that for ordinary carbon steels, alloy steels, and most other metals. Most metals form an oxide barrier on the outer surface, while stainless steels form a passive film. (see ref. 4, p. 550)

Passivity of stainless steels exists under certain conditions for particular environments. When conditions are favorable for maintaining passivity, stainless steels exhibit extremely low corrosion rates. (see ref. 4, p. 550)

From a phone call; dated Feb. 7, 1989; with David Hill at Sundstrand, he stated that the stainless steel in the brassboard was "passivated" to increase corrosion resistance. Passivation is performed for the following reason. During handling and processing operations, contaminants may be embedded in or smeared on the surfaces of the stainless steel. These contaminants may reduce the effectiveness of the passive oxide film that naturally forms on the surface of the

stainless steel. Passivation removes free iron, oxides, and other surface contamination which can accelerate corrosion. The treatment dissolves the embedded or smeared contaminants and restores the original corrosion-resistant surface, and maximizes the inherent corrosion resistance of the stainless steel. (see ref. 4, p. 550, 552)

5.2.1 Intergranular Corrosion of Stainless Steel

Despite the passivation of the stainless steel, there can remain some corrosion of the stainless steel metal. Stainless steels are susceptible to several forms of localized corrosive attack. Stainless steel can exhibit pitting, crevice corrosion, intergranular corrosion, and others. There is some indication that the stainless steel might be attacked by Intergranular Corrosion due to a non-uniform composition of the stainless steel constituents found in the debris (see Table 2). (see ref. 4, p. 547, 550, 553, 554)

Due to the very low percentage of chromium in the debris while containing a high percentage of the other constituents of the stainless steel, it is believed that the stainless steel is preferentially attacked at chromium depleted regions that often exist in austenitic stainless steels. Intergranular corrosion can affect alloys that are highly resistant to general and localized attack -- 300- and 400-series stainless steels and austenitic higher-nickel alloys. The susceptible stainless steels are those that have normal carbon contents (generally $>0.04\%$) and do not contain carbide-stabilizing elements such as titanium and niobium. This includes both types 304 and 316 stainless steel, both of which are extensively used in the brassboard. (see ref. 4, p. 324, 325)

Intergranular corrosion is a preferential attack at the grain boundaries within the material and is generally the result of sensitization. Sensitization occurs when grain-boundary precipitation of carbide, nitride, or an intermetallic phase occurs without sufficient time for chromium diffusion to fill the locally depleted region. The chromium-rich grain boundary is not the point of attack; instead, the chromium-poor region adjacent to the precipitate is attacked. The chromium-depleted regions have increased susceptibility to other forms of corrosion also, such as pitting, crevice corrosion, and stress-corrosion cracking. (see ref. 4, p.554)

Resistance to pitting and crevice corrosion of stainless steel is primarily controlled by the quantity of chromium and molybdenum in the metal. Higher chromium and especially higher molybdenum grades are more resistant to pitting and crevice corrosion. Molybdenum is especially effective in increasing resistance to pitting and crevice corrosion. Molybdenum in combination with chromium is very effective in stabilizing the passive film in the presence of chlorides. (see ref. 4, p. 549, 550, 554)

However, intergranular corrosion of the stainless steel in the brassboard has not yet been proven. Intergranular corrosion is believed to have occurred, based on circumstantial evidence only. The presence of intergranular corrosion cannot be confirmed without the removal and analysis of stainless steel brassboard components. The component would need to be opened for visual inspection of the grain structure, with the appropriate equipment, to visually verify that intergranular corrosion of the stainless steel has taken place.

6.0 CONCLUSIONS

There are a number of conclusions to be made from this study and they are as follows.

1. The plugging of the filters appears to be an on-going process.
2. The aluminum and stainless steel in the brassboard do appear to be corroding.
3. The debris collecting in the filters appears to be corrosion by-products from a corrosive attack on the metals in the brassboard.
4. The aluminum and stainless steel both exhibit localized attack of the metal, and not general uniform corrosion.
5. The aluminum is being pitted ("Pitting" --a form of corrosion).
6. The stainless steel appears to be preferentially attacked, possibly by Intergranular corrosion ("Intergranular Corrosion" --a form of corrosion).
7. The mechanism for the corrosion of the two metals is believed to be a galvanic coupling between the two dissimilar metals causing Galvanic Corrosion (Note: "Galvanic Corrosion" is a misnomer; it is not a form of corrosion, but a mechanism of corrosion) (see ref. 4, p. 234).
8. The corrosion mechanism, Galvanic Corrosion, can only occur when the ammonia in the system is contaminated, creating an electrolyte medium that can conduct electrons.
9. The common electrolyte is believed to be produced by water and chlorine, which entered the system through operation and servicing the brassboard.

10. Water entered the system because it is not air tight and due to possible leakage past an O-ring seal in condenser #2.
11. Aluminum and stainless steel are not compatible in an ammonia environment when combined in a system, except when under ideal conditions (ie. with absolutely pure ammonia).
12. Due to clogging of the filters, aluminum and stainless steel are not adequately compatible metals under normal and/or extreme operating and servicing conditions.

One must be keenly aware of the acceptable design criteria for each corrosion situation. Particularly, acceptable corrosion rates are not absolute, but vary from one application to another -- an acceptable corrosion rate for a material in one application, may not be acceptable in another.

In general, the corrosion problem with the brassboard is not a concern for a loss of material, ie. something that will eventually produce a hole and cause a leak, as in many applications of corrosion engineering. The rate of material loss appears to be quite small in comparison to the large amount of exposed surface area. Instead, the concern is for the amount of oxidized material that accumulates and clogs the brassboard filters, necessitating de-servicing to remove the residue.

Although aluminum and stainless steel in ammonia may be given a good corrosion resistance rating in tables, with little material loss, neither appears to have adequate corrosion resistance while operating under the current operating conditions. This design situation can occur for the following reasons. (1) The corrosion tables give corrosion data for very precisely controlled situations that test the effects of one corrosive mechanism, and generally do not attempt to quantify the effects of multiple mechanisms due to the innumerable combinations that can exist. (2) A design is made from the available resources at the time, and often does not include laboratory tests or documented field experience in comparable environments to aid the engineer in making design considerations. This is particularly valuable in the field of corrosion engineering where often the only way to obtain quantitative results is from actual laboratory tests or from field experience. (3) It is important to consider more than the ideal operating conditions. It is important to consider idle time, servicing, and reasonable variations from ideal operating conditions also.

In summary, it is important to characterize the probable service environment, and any reasonable deviations that might occur from the ideal operating conditions. "It is not [always] enough to consider only the design conditions. It is also necessary to consider the reasonably anticipated excursions or upsets in service conditions" (see ref. 4, p.547).

7.0 RECOMMENDATIONS

7.1 Material Selection

From the extensive use and experience with ammonia refrigeration systems by the personnel at Clay's, the following design recommendations are given.

To most effectively eliminate the corrosion problem in this type of ammonia refrigeration system, it is recommended that the ammonia be treated as a corrosive electrolytic agent for design purposes due to unanticipated anomalies in operation and servicing conditions as has been demonstrated. This is done since contaminants might enter the system during routine servicing and maintenance making the ammonia a corrosive agent. In this event, aluminum and stainless steel are not deemed sufficiently compatible. A change in material selection could be of invaluable worth for future designs.

A change ought to be made to have only one metal in the ammonia system -- titanium, aluminum or stainless. Since aluminum is heavily attacked by halide ions (group VII) and particularly by chlorine, it is recommended that titanium or stainless steel be used exclusively, where ever possible, for parts in contact with the ammonia. Types 304 and 316 stainless steel are currently used in the system. Type 304 stainless steel is adequate, but type 316 is preferred since it has better corrosion resistance due to the addition of molybdenum as an alloying element. This change in materials should eliminate the corrosion problem by eliminating almost all the dissimilar metals in the system (note: carbon bearings may remain in the principally stainless steel system).

7.2 Elimination of potential leak sites

The primary cause for concern is from contaminants entering the ammonia system. This is primarily caused by the fact that the brassboard is not air tight. There are hundreds of fittings, bolted flanges and plates, and O-rings. Each of these being a possible leak source for moisture or facility coolant to enter into the system when evacuated.

The key to this problem is to remove as many possible sources for a leak. One, it is recommended that all joints be welded except where necessary to remove parts for routine maintenance, such as filters. This would eliminate hundreds of potential leak sites. In the event of needing to remove a welded component, the piece can be cut-out with a tube cutter and then replaced by tig-welding a new piece with an automatic tube welder. Two, it is recommended that condenser #2, a flat plate condenser, be electron beam welded since it is a passive device and would not ordinarily require disassembly. In the unlikely event of requiring disassembly, the old one could simply be replaced with a new complete unit. Three, replace all EPR (ethylene-propylene) O-rings with Neoprene O-rings for their greater resilience, lower thermal coefficient of expansion, and lower gas permeability.

7.3 Eliminate Contaminants

It is also recommended that all water and other possible contaminants of the ammonia be avoided. For an aid in monitoring any contamination that might enter and possibly accumulate in the system, a Conductivity meter and/or a pH meter with a remote sensor could be used. This would help measure the corrosiveness of the environment and give a qualitative measure of the rate of corrosion in the system. It is also recommended that freon not be used to clean any of the components since it is a source of corrosion.

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16. Abstract There was a fine gray powder clogging the brassboard filters. The powder appeared to be residue from a galvanic corrosive attack by ammonia of the aluminum and stainless steel components in the system. The corrosion was caused by water and chlorine that had entered into the system and combined with the ammonia. This combination made an electrolyte and a corrosive agent of the ammonia that attacked the metals in the system. The corroded material traveled through the system with the ammonia and clogged the filters. Key conclusions were: the debris collecting in the filters is a by-product of galvanic corrosion, the debris is principally corroded aluminum and stainless from the system, and galvanic corrosion occurred from water and chlorine that entered the system during normal and/or extreme operating and servicing conditions. Key recommendations were: use only one metal in the ammonia system-titanium, aluminum or stainless steel, make the system as air-tight as possible-replace fittings with welded joints and replace EPR O-rings with Neoprene O-rings, and do not use freon to clean system components.			
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